Water Quality Management Practices

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Week – 02

Lecture – 06

Collection and Preservation of Samples and the Measurement of pH, Acidity, Alkalinity

Welcome everyone, welcome to this NPTEL online certification course on Water Quality Management Practices. My name is Gaurav, Professor Gourav Dhar Bhowmick. I am from the Department of Agricultural and Food Engineering of Indian Institute of Technology, Kharagpur, India. So, welcome to the second module. In this particular module, we will be majorly discussing about the quantity estimation of major pollutants starting with the lecture 1 on the collection and preservation of samples and the measurement of pH, acidity and alkalinity. If you see the concept that I will be covering majorly in this lecture module in this particular lecture video is the types, quantity and the preservation of sample.

The quality control and the result expression and the measurement of pH, acidity and the alkalinity. As you already know that whenever we talk about the wastewater treatment scenario or the wastewater treatment or wastewater or water whatever it is before even going ead with designing the plant or before even going ead with the necessity of treatment that it requires, we first need to understand that what are the different pollutants or what are the different what are the characteristics of the water or the sample or the wastewater that we are talking about, what are the characteristic of it like physical or chemical characteristics of those. In order to understand that physical or chemical or the biological characteristics of those, what we need to do? We need to take the do the sampling. So, there are scientific ways of doing this sampling procedure.

We cannot just simply go and take the sample from anywhere and we can consider it as . So, we have the samples let us do the analysis. We first need to understand the scientific way of collecting the sample from the sources. It can be municipal source, it can be industrial source, it can be surface water body from where the water is actually coming to you your your glass. So, whatever it is so, you just need to understand that what are the different type processes scientific way of collecting the sample whenever we will be doing some analysis for the treatment plant design or for say like any other purposes.

In general what are the objectives of sample collection? Major objectives are to collect in a small volume of water or the wastewater that is convenient enough to be transported back to the lab right or the testing facility that has to be our prior considerations that it has to be small enough just optimal amount. So, that we can easily carry to our lab facilities or the or the testing facilities. It the small volume of water which the sample that is collected it has to be accurate enough to represent the larger volume of the sample or the testing site from where it is being sampled that is very important that your sample has to be representative sample. It cannot be some random sample it has to be representative to the criteria for which you are actually using for at the for the place for the space or for the locality or for the like the water body for which you are actually using for. The sample must be handled carefully to prevent any compositional changes before performing the test.

This is the most important point that whenever you will be carrying the water or the water wastewater sample from the source to the laboratory facility or select testing facility you have to make sure it it does not change its compositions. Compositions in term in terms of its say like its physical compositions, chemical compositions, biological compositions whatever it is it should not be changed. How we can make sure that it will not change that is that is why the there is the picture of the scientific sampling thing is coming in coming . So, we need to be sure that the sampling procedure is scientific enough. In general what we do we suppose here take a container glass container or in like plastic container also we can take in case it is not available glass container we just go there we will rinse the container 2 3 times with the sample itself.

So, that it will not be having any kind of foreign particles present inside of it. After rinsing then we take the sample once the representative sample is collected we normally have to label it with a tag it is very important the labeling is very important. So, that you will not forget that the where actually you to the sample from. So, when we talk about the labeling it can be with the number it can be with the lat long or the latitude longitude it can be with the the time it can be with the sampling number or the place or the it is altitude or it is the the it is particular control lining numbering if you have done. So, in this in this case control lining numbers.

So, there are different things can be done. So, at different places so, we normally use the same fundamentals can be utilized for other sampling procedures as well, but basically we are talking about here the water samples. So, after you put the label or the say like the tag on the top of it what we need to do we need to be make we need to make sure that the lines should be flushed sufficiently to ensure that it is a representative sample. So, now, when we talk about the types of sampling the first thing come into our mind is the grab sampling or the catch sampling. What is the grab sampling? The grab sampling is nothing, but the the it is collected when you go to a certain place of your concern or the source you just simply take the sample in a bottle at a particular time and a particular place.

It should represent the composition of the source at that time and at that place of the sampling . So, this is called the grab sampling. So, grab sampling is done when the wastewater quality is known to be fairly constant in composition over a considerable period in all direction, then only we will go for grab sampling. In case of variations in quality and the flow with time the sampling at intervals or separate analysis is useful. We will discuss about it why we need to do this sampling in interval and what is it called which is different.

So, in general individual sampling when we go for this kind of setup we go we call it grab sampling. What is the composite sampling then? It is a mixture of grab sampling from a same sampling point at a different times of the day as I was mentioning. From the same point you are doing it at a different times of the day at the different at a certain interval. This is called the composite sampling. This is normally used in observing the average concentration and estimating the organic loading or the efficiency of a wastewater treatment unit.

How it is possible? Just imagine you have a treatment plant. There is a wastewater coming with say like 200 milligram per liter of BOD. Your plant is designed in such a way that it can treat up to 75 percentage of the BOD in it. However, with time how we can be sure about it? Whenever the effluent line whatever the effluent line is there you go there and you take the sampling from the from the supernatant point where it is actually going out of the system or you can get it collected from outside also. So, this is like with time at different time

interval you collect that effluent and you check the BOD value and you have to be in order to make sure that your treatment plant is actually treating the 75 percent of the BOD.

If you check that in the final BOD is always say like 50 milligram per liter so that means, from 200 milligram per liter it becomes always 50 milligram per liter that means, 75 percent removal efficiency can be witnessed from your design. So, in order to make sure the efficiency of a wastewater treatment unit you have to do the you can do the composite sampling . There is another type of sampling called integrated sampling. Integrated sampling when you are not sure that the pollutant composition all over the source is same. So, at the same time you take sample from different places .

So, when you take the sample from different points at the same time it is called the integrated sampling. In this integrated sampling mostly it is a fairly constant in composition over a considerable period in all direction you consider and also the you have to have a prior knowledge about the volume, movement and the composition of the various parts of the water which is to be sampled and it is it is very much necessary for you to understand that . So, what is the quality? We discussed about the three type of sampling grab sampling, composite sampling and the integrated sampling. So, what about the sample quality? In general 2 to 3 litre sample volume is sufficient for general chemical analysis. However, you have to make sure the same sample you are not supposed to use it for chemical, bacteriological or microscopic examinations as the collection handling and preservation techniques and the methods will be different for all of them.

Sample preservation techniques. So, once you done with the sampling you need to preserve it right. So, there are different preservation techniques which are available. In general preservation techniques it takes care of the chemical and the biological changes that continue after the sample is collected from the source. Different ions of aluminum, cadmium, chromium, copper, iron, lead, manganese, silver and zinc are subject to be lost in adsorption on the walls of this glass container.

How we can get rid of that phenomena? How we can get rid of this issue? So, we normally like collect the samples at different screen bottles and we acidified it using the concentrated hydrochloric or the nitric acid to a pH below 2.0 to minimize the precipitation and adsorption on the glass walls . This is one way of troubleshooting this issue. Other than that the temperature, pH, concentration of dissolved gas also change in a very short duration after the storage.

So, we cannot. So, it is very important if you want to take the sample, take the reading for temperature, pH and the concentration of dissolved gas you have to do it in situ . Colour order turbidity it may also increase and decrease with the presence of sulphite, sulphite, ferrous ions, iodide, cyanide which may lost through the oxidation process. So, colour order and turbidity has to be done within a hour or so, it is better or possibly on that place itself . Then the dependability of the water analysis also must relying on the experience and the judgment by the analyst also that is also very important . So, it comes with an experience.

Normally our standard procedure is we normally keep it in a freezer say at low temperature on 4 degree Celsius one of the best way to preserve most of the qualities of the sample until the next day. If you have some you add some preservatives it would be better. So, the even though preservatives are there, but still I think like it is better to as I mentioned the all the pH temperature dissolved or dissolved gases and all you can do it in situ. And preservation

methods majorly the pH control the chemical addition refrigeration the freezing are most suitable. So, that you can extend the period of testing time.

So, suppose your testing will start from the next day. So, to somehow make the sample ready or still available or still utilizable for whatever the test that will be doing in the next day. Majorly for determining the acidity and alkalinity the sample can be stored up to 24 hour not more than that for BOD within 6 hour you have to do the experiment. And for that 6 hour also you have to keep the sample in a refrigerated condition why? Because the organic decomposition will start taking place biological decomposition of the all the all the organic matter. So, once this biological decomposition of the organic matter will start taking place that the actual BOD value will be differing to the BOD value that will be tested or the analyzed .

So, this is the reason why you tend to be doing it within 6 hours of its collection. Analysis of temperature and pH I told you it should be done immediately of during the sample collection itself. And how we can still maintain the quality and the how we express the results? Normally we maintain the stipulated quality of analysis in the laboratory which should be represents the true quality of the water samples that is being analyzed. And how we can achieve this by definitely employing a trained and experienced manpower or the analyst should be very good and well trained and experienced using a good equipment facilities differ with different equipment with a more erroneous result can also be generated and which can actually drastically reduces the like the actual how say like the performance result that you are experiencing to the actual performance that is actually being experienced in the in the reactor itself and whatever the results will be getting will differ like anything.

So, this is not acceptable. You need to properly calibrate the instrument whatever if possible more frequently as frequently as possible like based on the type of instrument using the certified reagent and standard do not try to use something of low cost and also like just to go ead with some random chemicals and all you do not add it and at the end you will end up losing important samples and which sometimes may take may be very costly. There should be an interim quality control program which is to be carried out in routine basis at least once in a while to analysis of unknown samples. Quality of the laboratory to produce acceptable results should be analyzed and with by referencing the results from the external agencies also to do some kind of a validation of your study or validation of your results. The unit should be expressed in any kind of analytical results should be in milligram per liter in general we do it most of the pollutant present in the water or the waste water is normally being expressed in the terms of milligram per liter or parts per million which is also equivalent to milligram per liter or milligram per microgram per liter or say like percent when the concentration is greater than 10,000 milligram per liter. Milli equivalent per liter is also quite famous.

So, next is the pH. So, first water I would say like characteristics that we will discuss is the pH. The pH of the water or pH is majorly measured based on the water acid and base equilibrium achieved by various dissolved compounds mostly controlled by the carbon dioxide bicarbonate and the carbonate present in the system and it makes it is a it normally stays in its equilibrium conditions and actually presents the this the the the the the way it like you know represents the where the majorly the pH when we represent it is nothing, but it is a negative logarithm of the hydrogen ion activity present in your waste water or the water. When we do this acid based neutralization or water softening precipitation coagulation and disinfection or say like corrosion control process the pH really plays in a and very a very important role there and in the dilute solutions this hydrogen ion activity is approximately equal to the hydrogen ion concentration and we need to remember that the pH of the raw water sources should lie

between 6.5 to 8.5 due to the presence of the bicarbonate and carbonate of the alkaline earth salts and all.

So, majorly when we measure it for potentiometrically we use the indicating electrode or the glass electrode with the reference electrode with the standard buffer to get the actual value of pH for our sample. Other than that earlier days we use the litmus also for understanding the pH value of the water or waste water samples even now it is also pH it is like more of a crude method, but now this potentiometric methods are more accurate in in nature you can get up to the couple of decimal points also based on the type of potential type of you know pH meter that you have pH probe you have. Normally this electrodes we what we do this we by this electrodes we electrodes normally we after removing the storage solution we rinse it with the distilled water and dried it with the blotting paper and then the instrument is needs to be calibrated with the electrodes in the buffer solution. What we do we put the electrode once the electrodes are like we should be removed with time to time after the treatment is done and then rinse it properly and blot it dry and they immersed in a second buffer below the 10 pH level.

The reading should be within 0.1 units for the pH of the second buffer and then the same for sampling for actual sample analysis we have to establish equilibrium between the electrode and the sample by stirring the sample to ensure that the homogeneity is actually maintained when we will be measuring the pH. In general nowadays those instruments are they are coming with the self calibration processes and all in general they actually comes with a very quite they give us a very precise result. Then there comes the measurement of acidity, the acidity contributes to the corrosiveness or the influence the chemical reaction rates or the chemical specialization or the biological processes. The strong mineral acids or the weak acids such as carbolic acid, carbonic acid and acetic acid and the hydrolyzing salts such as the iron or aluminum sulfates it contributes majorly contributes to the acidity. If you can easily understand when we talk about the acidity it means the pH of the solution is less than 7 right.

So, there the presence of different dissolved oxygen, carbon dioxide and all should be handled clear fully. So, to prevent the loss of dissolved gases when suppose when we carry the sample from its sources to the to our laboratory. We have to also make sure that this the whenever we will be doing this analysis pH analysis and all that it is the concentration majorly it would be better if we do it in in situ and we can just take our what is it called this portable pH meter there itself and we can do it the sampling there itself. And then when we talk about the acidity in the sampling which are containing the carbon dioxide, bicarbonate and the carbonates it titration value pH of 8.3 at 25 degree Celsius. It majorly gives you a understanding about the weak acids that is present in the system and if it goes if you want to make sure that you to know the what the amount of how like how much acidic is it is like and if it is more than say like if it is less than say like 3.7. Then we go ead with the methyl orange acidity present with the presence of bromophenol blue is blue this chemical. So, major interference so, dissolved oxygen dissolved gas which is contributed to acidity and liquidity such as carbon dioxide, hydrogen sulfide, ammonia it may be lost or gain during the storage sampling or the titration procedure.

So, we have to be very cautious about that. So, which can actually drastically change the acidity value of its actual one that that is suppose supposed to be there. This losses can be minimized by titrating to the end point and avoiding vigorous shaking or protecting the sample from the atmosphere for like during the titration. And also occasionally cleaning the glass silo to prevent the coating of oily matter suspended solid or precipitates etcetera which may create

the sluggish responses. And do not use the indicator titration with the colored or tarbit samples that may also obscure the color change at the end point and you may end up getting some erroneous result. The procedure selection in general that we do the titration in the room temperature using a properly calibrated pH meter and electrically operated titrator and the color indicator.

We determine the sample acidity from the volume of standard alkali required to titrate a portion of a pH at 8.3 phenolphthalein acidity what we call and 3.7 which we call methyl orange acidity . So, sample size in general 20 ml or more would be better we take sufficient large amount of this titrate and then the samples are and having this acidity is less than 1000 milligram per liter of calcium carbonate. We select a volume of around 50 of with less than 50 milligram of calcium carbonate equivalent acidity and titrate it with 0.02 normal sodium hydroxide. While we assure that the it will be the acidity will be more than 1000 milligram then we do the acidity equivalent test with the less than 250 milligram of calcium carbonate and titrate it with the 0.1 normal of sodium hydroxide. After the titration of this acidity is done we this the acidity value of this water sample water whatever it is water or waste water sample can be easily expressed using this equation in milligram. Majorly the value will get it in a unit of $CaCO_3/L = \frac{(A\times B)-(C\times D)\times 50000}{mL\ of\ sample}$, where A is the ml of NaOH titrant used and B is the normality of that sodium hydroxide and C is the milliliter of sulphuric acid and D is the normality of the sulphuric acid and if acid is added for the preserving samples and all. Alkalinity, alkalinity is another important factor this acid neutralizing capacity of water can be easily find out using the alkalinity and also this acidity and alkalinity is very important when we have to make sure that certain type of reactions has to take place in your reactor and you have to maintain the certain alkalinity or acidity using some pH buffer and all.

So, this is a very important parameter that we need to understand. In general it gives us an measure of the aggregate of all the titratable bases present in the water and can be easily interpreted in terms of specific substances only when the chemical composition of the sample is known. The alkalinity is primarily because of the function of carbonate bicarbonate and the hydroxide content and it is taken as a indication of the concentration of this all this constituents. When alkalinity is due to the carbonate or bicarbonate the pH equivalence point of the titration is determined by the carbon dioxide concentration at that stage. But the at that time the colour changes by this metacrystalline purple at the pH of 8.3 and bromocrystalline green or the methyl orange and 4.5 it make thus indicator suitable for alkalinity titration. What are the procedures? In general we use the colour indicators that may be used for routine or control titrations without interfering the colour or turbidity. The sample size of around 50 25 to 50 ml of titrate we normally use and we in case of low alkalinity method we titrate it with 200 ml of sample with 0.02 normal sulphuric acid from a 10 ml burette. And standard sulphuric acid or hydrochloric acid of 0.02 normal is used for titration and the alkalinity can be estimated as a milligram of $CaCO_3/L = \frac{A\times N\times 50000}{mL\ of\ sample}$ which is A is nothing, but the volume of the standard acid that we used and n is the normality of that standard acid . So, in conclusion we we did a proper we understood that what are the necessity of the proper sample collection and why it is very important for us to do the sample collection in a very precise scientific manner otherwise we may end up having some erroneous result unnecessarily. Because suppose we are trying to get some sample and we try to test it for say like BOD or COD something else and we forget to keep it we keep it in our back side of your trunk or say like our car and we keep it for couple of hour and we once we come to our lab by that time with say like it is more than 6 7 8 hours by that time it will be enough time for the biological or the the organic matter present there which should start degrading

biologically. So, it may reduce the actual BOD value or actual COD value it can it may drastically change because of the considered vigorous shaking and all it may considerably change the acidity value of your sample it will change the pH because of that in case at the end you will see something very like the results which are not actually resembling to the one that should be there in the real cases.

And we also discuss about the preservation techniques to safeguard ourselves with that we discuss about how we can actually control the pH we can do the temperature control there itself we can carry some ice bags during the sample collection. And we most of the experiments which can be done in situ which should be doing in the in situ itself and some of the some of the cases in like mineral mineral adsorption and all on the glass bottle in order to reduce it we can use the hydrochloric acid or say at a certain pH and only less than 2 pH and all will be better and a couple of drops should be provided. So, that it will not let it how to say the decomp a adsorb on the surface of the glass walls all those minerals and all. Internal quality control programs are necessary to ensure the quality testing and compliance with the standards and the regulations.

We need to train and the analyst and there. So, the analyst should be like have proper training, proper experience and has a proper judgment mentality. So, that it will be very much crucial for us to prove that the whatever the results that we are getting out of the water quality parameter testings are actually deterministic to the actual real wastewater from the source itself. So, it is very it is quite important that it comes with the experience and the analyst has to be experienced enough to actually come to a conclusion that . So, the pH value is this so that means, the pH value is this there would be no certain changes that you can expect from people to people. So, this is it this is the conclusion for this particular lecture video and these are the some of the references that we can follow.

So, majorly what we discussed here will be I will be continuing it in the next lecture video also where I will be discussing majorly about difference or the solid concentration and the presence of different type of solid in the wastewater and how it can determine those. And, then we will be discussing about the biological oxygen, biochemical oxygen demand, chemical oxygen demand, total organic carbon etcetera and their relationship and how we can actually do the BOD modeling which are very important. So, in this whole module I will be majorly discussing about the different type of pollutants present in the wastewater and that has to be that you should know so that in future when we will be designing it will be much easier for you to go ead with the those informations .

So, that is it. Thank you so much . We will see you in the next video.